VISIBLE ABSORPTION BANDS OF MERCURY HALIDES HgCl, HgBr AND HgI

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Plate XI

ABSTRACT. The absorption bands of HgCl, HgBr and HgI have been obtained by heating the substance in an open steel tube to a temperature of 1100°C. In HgCl and HgBr the band systems have been measured and a vibrational analysis is suggested. From the values of the constants, the heats of dissociation of these molecules in the upper and lower electronic states have been determined.

INTRODUCTION

The importance of the study of absorption spectra is well known. In the case of atoms and molecules, in the former of which lines and in the latter band absorption is obtained, the ground state of absorption is known to be the normal state. In certain molecules, *e.g.*, oxygen and the halogens,[1] converging progressions of absorption bands are obtained from which their heats of dissociation, could be directly determined. In other molecules, such as sulphur and phosphorous,[2] the absorption bands show diffuseness of the heads or their sudden absence abruptly in a sequence, indicating what is known as the phenomenon of pre-dissociation. In all cases the absorption spectra are considered to be providing valuable data concerning the molecules involved. The author has therefore undertaken the investigation of the absorption spectra of the halides of various elements, particularly those of high atomic weight, the ground states of which have either not been determined at all or have not been determined from the study of absorption. In the course of such an investigation with the halides of mercury, absorption bands have been obtained characteristic of the molecules, lying in the visible region, which do not appear to have been recorded till now. It is the purpose of the present paper to give details of these results, a short report of which has appeared in Current Science.[3]

EXPERIMENTAL

The procedure adopted in obtaining the absorption spectra consists in heating the substance in a seamless steel tube about 50 cms. long and 5 cms. in diameter, open at both ends. In the first experiments a similar tube closed at both ends by glass or quartz windows protected by water-cooled jackets was used. The

tube was exhausted continuously by a Cenco Hyvac pump and the substance was heated. But, in spite of the protecting water jackets, the substance got deposited on the windows almost instantaneously and prevented all further examination. The open tube was found very useful and extremely simple to operate.

Different temperatures had to be tried before any absorption bands were observed. Two furnaces were employed—an electrical furnace capable of heating the tube up to 800°C and a specially constructed coke furnace, through which a powerful blast of air from a motor blower could be steadily maintained. By replenishing the coke at intervals, temperatures of the order of 1200°C could be easily attained. An exact measurement of the temperatures was made by the use of a standardised direct-reading optical pyrometer. At the temperature of the electrical furnace (about 800°C) no bands were observed. Using the coke furnace the characteristic bands made their appearance. There was observed also that an optimum temperature was necessary for the excitation of the bands—determined by the pyrometer to be about 1000-1100°C. Due to the need of replenishing the substance every two or three minutes, it was not found practicable to use a spectrograph of very high dispersion. The instrument used was of the Fuess type of large light-gathering power giving a dispersion of about 20 Å per mm. at λ4400. Effective exposures of about ten minutes were given: larger exposures often obliterated the appearance of the bands, due probably to the above condition of an optimum temperature for the excitation of the bands. The source of continuous spectrum was a hundred-watt projector lamp. Ilford Special Rapid panchromatic plates were used and the spectra were measured by a Hilger comparator using iron standards and a simple Hartmann dispersion formula.

Absorption spectra of various other salts of mercury were also photographed to make sure that the reported bands could be ascribed, from an experimental basis, as due to the particular halide, chloride, bromide or iodide that was worked with. Bands were obtained only with the above three halides and with none of the other salts tried—*e.g.*, the fluoride, sulphide, oxide and the nitrate—all of which were attempted, under identical experimental conditions.

RESULTS AND DISCUSSION

Mercuric Chloride.—In emission, the band systems of HgCl have been previously investigated chiefly by three workers. Wieland[4] divided the characteristic bands into three classes—Class III occurring in the visible region and the other classes in the ultra-violet. He reported the analysis of Class I system. Cornell[5] and more fully Sastry,[6] investigated the Class II system and reported a complete vibrational analysis. The visible bands are yet to be measured accurately before an analysis can be attempted. The absorption bands obtained in the present work lie in the region from λ4900 to λ4100 which is a portion of the extended region in which the visible emission system is reported to lie.

Absorption bands of mercury halides.

(a) HgCl, high temperature.

(b) ,, low temperature.

(c) HgBr

The latter system was also reported to be very complex and diffuse and for that reason perhaps could not be analysed. The writer believes that the absorption bands recorded in this paper are part of the emission system, involving the lower vibration quantum numbers. In general appearance they resemble the Class II system analysed by Cornell and Sastry. They consist of sequences of distinct doublet bands. Three of these sequences $\Delta v = 0, \pm 1$ in the region $\lambda 4500$ to $\lambda 4250$ are well developed. The very disposition of the heads, as can be seen from the reproduction (plate XI), suggest that they ought to form long sequences giving a narrow Condon parabola. They are thus ascribed to the diatomic molecule HgCl. Table I contains the wave-lengths of all the band heads measured on the plate and are given only correct to the nearest Angstrom unit. The doublet at $\lambda 4876$, $\lambda 4842$ could be measured with difficulty. The wave numbers are found from Kayser's Schwingungzahlen and the intensities are visual estimates. The various heads could be arranged in a diagonal array, the most intense of the heads being assumed as the (0,0) band. The quantum numbers assigned to each head are shown in the last column of the table. It will be seen that the bands consist of doublet heads, the two components having been designated as the Q_1 and Q_2, the doublet interval having an average value of about 120 units of wave number. The other alternative of assigning one of the component heads as due to isotope Cl^{35} and the other component to the isotope Cl^{37} cannot be possible on account of the relative intensities of the component heads. If they are due to the isotopes, the intensities of the heads should be in the ratio of 3 : 1, the abundance ratio of the two isotopes of chlorine. The failure to detect the isotopic head might be due, as in the Class II system of HgCl studied by Cornell and Sastry, to its overlapping with the next or the previous band head in the sequence.

Of particular interest to the chemist is the estimate of the heats of dissociation of molecules. For this purpose an approximate formula has been found to fit the band heads contained in Table I. It must be stated, however, that owing to the small dispersion used, there are large discrepancies in the intervals of the vibrational levels and hence the formula must be considered approximate. For the Q_1 heads the formula is

$$\nu = 22978 + [399(v' + \tfrac{1}{2}) - 4(v' + \tfrac{1}{2})^2] - [436(v'' + \tfrac{1}{2}) - 7(v'' + \tfrac{1}{2})^2]$$

the coefficients of $(v' + \frac{1}{2})$ and $(v'' + \frac{1}{2})^2$ in the above equation, according to the usual relation

$$D' = \frac{\omega'^2_e}{4x'_e\omega'_e} \times 8106$$

give the value of D', the energy of dissociation of the initial electronic state of the molecule. Similarly D'', the energy of dissociation corresponding to the lower electronic state can be obtained. The values, expressed in electron volts, are

$$D' = 1.1 \qquad D'' = 0.8.$$

Mercury Bromide.—The absorption bands obtained in the case of mercury bromide, extend between λ5000 and λ4000. About fifty heads have altogether been measured. These have been arranged into five sequences, $\Delta v = 0, \pm 1, \pm 2$. Another sequence is also indicated, a few bands remain unclassified. A catalogue of the wave-lengths, wave numbers and intensities of the band heads is shown in Table II in which the last column gives the classification. Here again, in deriving the vibrational assignments, the strongest band is assumed to be first

TABLE I

Absorption Bands of HgCl

Wave-length A. U.	Int.	Wave number	Classification v', v''	
4876	0	20503	0, 0	Q_1
4842	0	20647	0, 0	Q_2
	0	20142	0, 2	Q_1
4493	1	22251	0, 2	Q_2
4447	1	22481	4, 5	
4443	2	22501	3, 4	
4439	1	22521	2, 3	Q_1
4437	3	22531	1, 2	
4434	3	22547	0, 1	
4418	1	22628	3, 4	
4416	2	22639	2, 3	Q_2
4415	2	22644	1, 2	
4412	3	22659	0, 1	
4371	1	22872	4, 4	
4368	1	22887	3, 3	
4365	1	22914	2, 2	
4359	2	22935	1, 1	Q_1
4355	3	22955		
4354	5	22961	0, 0	
4346	1h	23003	5, 5	
4344	1h	23011	4, 4	
4342	1h	23024	3, 3	
4340	1h	23035	2, 2	Q_2
4337	1h	23051	1, 1	
4334	4	23067	0, 0	
4301	2	23244	5, 4	
4296	3	23271	4, 3	
4292	3	23293	3, 2	Q_1
4287	4	23320	2, 1	
4281	3	23352	1, 0	
4264	1	23445	4, 3	
4262	2	23456	3, 2	Q_2
4261	2	23462	2, 1	
4259	3	23473	1, 0	
4211	1	23741	2, 0	Q_1
4191	1	23854	3, 1	Q_2
4187	1	23877	2, 0	

h means hazy

TABLE II

Absorption Bands of HgBr

Wave-length A. U.	Int.	Wave number	Classification v', v''
4957	1	20168	—
4886	1	20486	—
4816	1	20748	—
4491	2	22260	5, 7
4484	2	22295	4, 6
4479	2	22320	3, 5
4473	2	22350	2, 4
4467	2	22380	1, 3
4462	2	22405	0, 2
4420	3	22618	3, 4
4413	3	22654	2, 3
4408	3	22679	1, 2
4401	3	22716	0, 1
4381	1	22819	—
4379	1	22830	6, 6
4373	1	22862	5, 5
4366	1	22898	4, 4
4361	1	22924	3, 3
4355	2	22956	2, 2
4346	3	23003	1, 1
4341	5	23030	0, 0
4321	3	23136	—
4300	4	23200	4, 3
4301	4	23244	3, 2
4295	4	23276	2, 1
4289	4	23309	1, 0
4273	2	23396	—
4263	2	23451	—
4256	2	23490	5, 3
4251	2	23517	4, 2
4246	2	23545	3, 1
4239	2	23584	2, 0
4230	1	23634	—
4220	1	23690	—
4210	1	23746	6, 3
4204	1	23780	5, 2
4197	1	23820	4, 1
4165	1	24002	—
4162	1	24020	—
4160	1	24032	—
4112	1	24312	—
4081	1	24497	—
4066	1	24587	—

member of the $\Delta v=0$ sequence. The following formula has been obtained for the band heads; as in HgCl, this too must be considered as an approximate one.

$$\nu = 23057 + [267(v'+\tfrac{1}{2}) - 1(v'+\tfrac{1}{2})^2] - [324(v''+\tfrac{1}{2}) - 5(v''+\tfrac{1}{2})^2].$$

The values for D′ and D″ are obtained to be

$$D' = 2.2 \text{ volts}$$

$$D'' = 0.7 \text{ volts}.$$

Mercury Iodide :—With this substance in the tube the absorption bands of iodine in the red have been obtained intensely; in addition to these only a few band heads about a dozen have been obtained in the region $\lambda 4600 - \lambda 4100$. They are however feebly developed and the system is thus only incompletely photographed. Further investigation of the bands is necessary. The wave-length data of the bands are, hence, not reported in this paper.

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